MOLECULAR MECHANICS STUDIES OF ENTHALPIES OF FORMATION AND STRAIN ENERGIES OF AZOXYALKANES

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Abstract

A force-field has been developed, on the basis of available experimental and PRDDO data, to permit molecular mechanics calculations on azoxyalkanes. The calculated structures and enthalpies of formation are in fair agreement with experimental results. The calculated enthalpies of formation and strain energies are compared with the corresponding quantities for analogous azoalkanes.

Introduction

The thermal stability of azoxy compounds ($-\overset{\delta-}{N}-\overset{\delta+}{N}(\rightarrow O)-$), stands in stark contrast to that of the azo analogues (-N=N-).[1] The relative rate of nitrogen extrusion vs. the corresponding loss of nitrous oxide is in the order of 10^{17} at 298.15 K. The corresponding ΔE_a, larger than 23 kcal mol^{-1}, is remarkably large for two processes differing formally only by the N-oxide perturbation. In order to get a better understanding of the origin of this large difference in stability, thermochemical data for azo and azoxy compounds are needed. Enthalpies of formation for some azoalkanes have been reported[2, 3] and azoxyalkanes have been studied by combustion and vaporization calorimetry in this laboratory.[4, 5] However, only a few enthalpies of formation refer to directly comparable structures.

The molecular mechanics method (MM)[6] has been shown to be a fast and efficient way of calculating enthalpies of formation for a variety of organic compounds, usually in fair agreement with experimental results. The aim of the present work was to extend the study of azo N-oxides to a development of a force-field, which could calculate enthalpies of formation and strain energies of azoxy compounds, and to compare the results with those of structurally related azoalkanes.

A draw-back of molecular mechanics is that, since it is an empirical method, a large amount of accurate structural and thermochemical data are needed for a given class of compounds before the method can be applied. Since the available structural data for azoxyalkanes are very limited, PRDDO † energy minimized geometries were used together

† partial retention of diatomic differential overlap (see reference 7)

with experimental results in the force-field parametrization.

The molecular mechanics method

The Allinger 1973 force field (MMI)[6] was used as a starting point for the study of azoxy compounds. The hydrocarbon parameters[8] were used together with some additional parameters needed to deal with the azoxy functional group. The force field parametrization of azoalkanes by Kao and Huang[9] served as a basis in the development of azoxy parameters. The force-field parametrization was based on X-ray structures of three *cis*-azoxyalkanes[10, 11] and PRDDO calculated structures of *trans*- and *cis*-azoxymethane.[12] The values settled upon are listed in Table I.

The nitrogen lone pair was considered in the parametrization of azoalkanes and for that reason was included in this work. The oxygen, on the other hand, was represented as spherical, ignoring its lone pairs, since they were not accounted for in the carbonyl force field.[8]

The van der Waals parameter for the nitrogen lone pair, together with the natural bond length, stretching force constant and the dipole moment of the $N_{sp}2$ -Lp "bond" were given the same values as in azoalkanes. The stretching force constant and the dipole moment of the nitrogen-oxygen bond were taken equal to the corresponding parameters for the carbon-oxygen double bond in carbonyl compounds.[8] The dipole moment of the other bonds (C-N, C-N(O), N-N) were estimated from charge densities given in reference 11.

As a first approximation, the N(O) atom was treated as an azo

nitrogen, with the exception of the positive charge and the bond to the oxygen atom. Numerical values for the necessary stretching and bending parameters were taken directly from the azo force-field. The stretching parameters for the two C-N bonds and the bending parameters for the CNN(O), CN(O)N, CNO and NNO angles were varied separately by trial and error, until a reasonable overall agreement with X-ray and PRDDO structures was obtained. The V_1 term of the CNNC torsion was adjusted to fit the experimental results for the enthalpies of formation of some *trans* and *cis* azo N-oxides.

Results and discussion

Structures

The X-ray structures of two asymmetric *cis*-azo N-oxides, differing in the position of the oxygen, have been determined.[10] Recently, an X-ray determination of the molecular structure of 2,3-diazabicyclo [2.2.2] oct-2-ene N-oxide has been reported.[11] In Table II structural parameters for these three compounds are compared with those calculated by molecular mechanics. As can be seen from the table, experimental X-ray structures are reasonably well reproduced by the force field method. The largest differences are found for the C-N(O) distance in N-oxide 2 (0.050 Å) and the C-N bond length in N-oxide 3 (0.025 Å). However, the experimental values for these parameters are not consistent with the corresponding bond lengths in the two other structures.

Table III contains MM and PRDDO optimized geometries of the *trans* and *cis* isomers of azoxymethane. The agreement between the two

methods is fairly good. The major discrepancies occur for the nitrogen-nitrogen bond lengths, which are probably overestimated by the PRDDO method.

Enthalpies of formation.

The major objective of this work was to develop a method for calculating enthalpies of formation of azoxy compounds. As previously described,[6, 8] the enthalpy of formation is calculated using the equation:

$$\Delta H^{o}_{f}(g) = \Delta H_{steric} + \Delta H_{bond} + \Delta H_{stru} + PFC$$

ΔH_{steric} refers to the steric energy of the molecule calculated by the program. ΔH_{bond} is the sum of bond enthalpy contributions and ΔH_{stru} refers to structural enthalpy contribution, i.e., correction terms for primary, tertiary and quarternary carbons. The last term, PFC, partition function contribution, contains conformational, torsional, translational and rotational contributions.

The enthalpy of formation parameters for the hydrocarbon parts of the molecules are taken from the 1973 force field.[8] The effect of branching at carbons next to the nitrogens is assumed to be the same as in azoalkanes. The structural enthalpy terms are therefore taken from the azo analogues, which in turn are identical to the corresponding alkane and alkene parameters. The enthalpy contributions from the C-N, C-N(O), N-N and N-O bonds are added to give a parameter accounting for the azoxy functional group. This enthalpy parameter was optimized to give the best fit of our experimental results. The enthalpy of formation parameters are given in Table IV. Table V

lists steric energies, together with calculated and observed enthalpies of formation of seven azo N-oxides. The general agreement between the available experimental and the calculated values is satisfactory, with an average deviation of 0.41 kcal mol^{-1}. This is slightly better than the results obtained for azoalkanes. We may conclude that in spite of the limited amount of existing experimental data on azoxy compounds, the developed force field can reasonably well reproduce enthalpies of formation.

The predicted enthalpies of formation for *trans*- and *cis*-azoxymethane are 14.50 and 20.50 kcal mol^{-1}, respectively. Thus, the enthalpy of isomerization for azoxymethane becomes 6.0 kcal mol^{-1}, while the PRDDO value is 9.9 kcal mol^{-1}.[12] No experimental results for the enthalpies of formation or isomerization have been reported.

A comparison of experimental enthalpies of formation of azo compounds and the corresponding N-oxides shows that the oxidation of the azo to the azoxy moiety is a highly exothermic process. However, among the existing experimental results for azo and azoxy compounds, only a few are for directly comparable structures. With the azo and azoxy force fields, it is possible to extend this comparison to compounds for which experimental information is lacking, and thereby get a better overall quantitative representation of the relative energetics of the azo and azo N-oxide heteroextrusion reactions.

Table V contains calculated $\Delta H^{o}_{f}(g)$ values for two *trans*- and six *cis*-azo and azoxy compounds, for which experimental results exist for one or both of the pair to be compared. In all cases the introduction of the nitrogen-oxygen bond lowers the enthalpy of formation by 15-20 kcal mol^{-1}.

Strain Energies

Strain energy is defined as the difference in enthalpy of formation of an actual compound and a hypothetical isomer, which is free of strain. The numerical value of the derived strain energy will depend on the choice of reference system. Thus, strain energies estimated from different bond energy schemes are not directly comparable.

In reference 5 strain energies of azo and azoxyalkanes based on existing experimental results were discussed. The enthalpies of formation for the reference compounds were calculated using an Allen bond energy scheme.[13] In the derivation of the necessary parameters, it was assumed that di-*n*-propyldiazene, di-*i*-propyldiazene, di-*t*-butyldiazene and di-*n*-propyldiazene N-oxide, all in their trans conformations, were free of strain.[4]

Allinger defines strain energy as the difference between the calculated enthalpy of formation and the enthalpy of formation of a strainless isomer.[6] The strainless enthalpy of formation, ΔH_f^s, is given by the expression:

$$\Delta H_f^s = \Delta H^s_{bond} + \Delta H^s_{stru} + TR$$

where ΔH^s_{bond} and ΔH^s_{stru} are the strainless bond and structural enthalpy contributions and, finally, TR refers to the translational and rotational contributions. As pointed out by Allinger,[6] the strain is in part caused by the presence of high-enthalpy conformations mixed in with the most stable conformation. Thus, in this work the strainless reference system was taken as the most stable conformations of the four compounds listed above. The strainless enthalpy parameters

given in Table IV were derived in such a way as to fit the experimental enthalpies of formation, corrected for conformational and torsional contributions. The strainless enthalpy parameters for the hydrocarbon part of the molecules were taken from reference 8. Derived strain energies are given in Table VII. The strain energies of the reference compounds, which are results of deviations between experimental and calculated values and also due to the presence of high-enthalpy conformations, are included for comparison. It should be pointed out that the reference compounds were all trans, which means that the strain energies of the *cis*-compounds refer to hypothetical *trans*-isomers.

The variation of strain energy vs. structure is similar for the two classes of compounds. In contrast to alkanes and alkenes, the five-membered azo and azoxy rings exhibit less strain than the corresponding six-membered rings. The compounds having quarternary carbons attached to the nitrogens exhibit on the average the largest differences in strain energies between azo and azoxy compounds. In reference 4 it was argued that the strain of di-*t*-butyl N-oxide could be a result of steric repulsions between the oxygen and the methyl hydrogens. However, an analysis of the calculated steric energy does not support this assumption.

Acknowledgements

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Table I Force-field parameters [a)]

atom	van der Waals parameter γ^*/A	ε/kcal mol^{-1}
N	1.700	0.039
O	1.650	0.046
Lp	1.200	0.025

Natural bond lengths and stretching force constants

bond	ℓ_o/A	k_ℓ/mdynA	dipole/D[b)]
C-N(O)	1.490	4.50	-0.30
C-N	1.450	3.50	1.75
N-N	1.257	10.72	2.05
N-Lp	0.500	4.60	0.60
N-O	1.270	10.80	2.60

Natural bond angles and bending force constants

angle	type[c)]	θ_o/deg	k_θ/mdyn A rad^{-2}
C-N(O)-N		115.40	0.38
C-N-N(O)		105.00	0.57
N-N-Lp		126.70	0.36
N-N-O		126.30	0.38
C-N-O		119.30	0.57
C-N-Lp		126.30	0.36
H-C-N	0	108.50	0.24
	1	108.51	0.24
	2	107.90	0.24
C-C-N	0	109.47	0.38
	1	110.51	0.38
	2	110.20	0.38
N-O	Out of plane	0.00	0.80
N-Lp	" " "	0.00	0.05

Torsion parameters (in kcal mol^{-1})

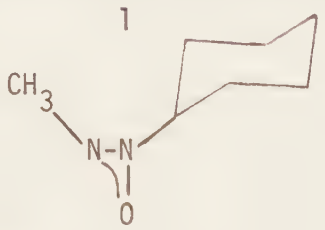
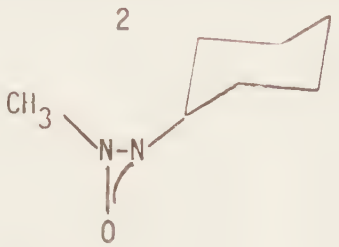
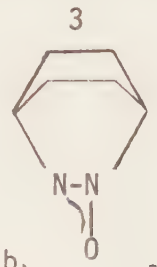
dihedral angle	V_1	V_2	V_3
$C_{sp}3$-N-N-$C_{sp}3$	-0.90	14.00	0.00
X-N-N-Y (X = $C_{sp}3$,O; Y = O,Lp)	0.00	14.00	0.00
X-$C_{sp}3$-$C_{sp}3$-Y (X = $C_{sp}3$,H; Y = N)	0.00	0.00	0.53
H-$C_{sp}3$-N-N	0.00	0.00	0.00
X-$C_{sp}3$-N-Lp (X = H, $C_{sp}3$, $C_{sp}2$)	0.00	0.00	1.95
H-$C_{sp}3$-N-O	0.00	0.00	-0.73
X-$C_{sp}3$-N-N (X = $C_{sp}3$, $C_{sp}2$)	0.00	0.00	0.70
X-$C_{sp}3$-N-O (X = $C_{sp}3$, $C_{sp}2$)	0.00	0.00	-1.75
$C_{sp}2$-$C_{sp}2$-$C_{sp}3$-N	0.00	0.00	0.30
H-$C_{sp}2$-$C_{sp}3$-N	0.00	0.00	0.53

a) For hydrocarbon parameters see reference 8.

b) The positive sign is defined as having the atom to the left at the positive end of the dipole.

c) The type refers to the number of hydrogens attached to the central atom.

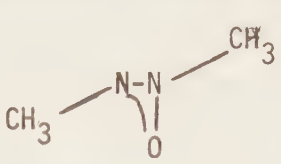
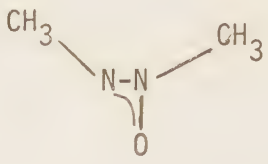
Table II Comparison between experimental and molecular mechanics structures.

parameter	1 		2 		3 	
	exp[a]	calc	exp[a]	calc	exp[b]	calc
N-N	1.253	1.264	1.262	1.263	1.266	1.261
C-N(O)	1.512	1.513	1.457	1.507	1.507	1.506
C-N	1.462	1.460	1.459	1.463	1.491	1.466
N-O	1.258	1.270	1.273	1.275	1.270	1.272
CN(O)N	126.0	126.3	126.2	125.0	119.1	117.3
CNN(O)	117.6	117.5	118.9	119.6	109.7	110.7
NNO	119.3	119.5	119.9	119.4	118.9	118.0
CNO	114.7	114.2	113.9	114.7	122.0	124.7
CCN(O)	109.0	109.7			106.4	107.2
CCN			107.5	106.8	108.9	109.3

a) Reference 10

b) Reference 11

TABLE III COMPARISON BETWEEN PRDDO AND MOLECULAR MECHANICS STRUCTURES OF *trans*- AND *cis*-AZOXYMETHANE.

				
PARAMETER	PRDDO[a]	MM	PRDDO[a]	MM
N-N	1.315	1.258	1.322	1.261
C-N(O)	1.504	1.502	1.500	1.502
C-N	1.462	1.460	1.459	1.456
N-O	1.286	1.271	1.289	1.275
CN(O)N	115.2	117.2	123.1	123.8
CNN(O)	111.5	110.8	114.7	115.2
NNO	118.3	117.8	122.2	120.9
CNO	126.6	125.0	117.8	116.7

[a] Reference 12

TABLE IV ENTHALPY OF FORMATION PARAMETERS (in kcal mol^{-1})

	C-N-N-C (O)	C-N=N-C	N-CH<	N-C<
Normal[a)]	41.99	54.90[b)]	-1.70[b)]	-4.83[b)]
Strainless[a)]	38.19	57.87	-3.37	-8.18

a) For definition and derivation see text.

b) Derived in reference 9.

TABLE V. COMPARISON BETWEEN THE CALCULATED AND THE OBSERVED ENTHALPIES OF FORMATION (in kcal mol^{-1})

Compound	steric energy	$\Delta H^{o}_{f}(g)$ calc	exp	calc-exp
trans-di-*n*-propyldiazine[c] N-oxide	2.69	- 7.20	- 7.41 (0.33)	+0.21
trans-di-*t*-butyldiazene N-oxide	3.28	-25.84	-25.71 (0.50)	-0.15
1,2-Diaza-3,3,6,6-tetramethyl-cyclohex-1-ene N-oxide	12.01	- 6.37	- 6.33 (0.55)	-0.04
2,3-Diazabicyclo[2.2.1] hept-2-ene N-oxide	14.00	30.66	30.55 (0.34)	0.11
2,3-Diazabicyclo[2.2.2] oct-2-ene N-oxide	11.62	21.39	22.08 (0.44)	-0.69
2,3-Diazabicyclo[2.2.2] octa-2,5 diene N-oxide	13.88	53.95	52.82 (0.51)	1.13
6,7-Diazabicyclo[3.2.2.$0^{2,4}$] non-6-ene N-oxide	15.19	53.50	54.04 (0.45)	-0.54

[a] Experimental $\Delta H^{o}_{f}(g)$ taken from reference 4 or 5.

[b] The figures in parentheses are twice the overall standard deviations of the means.

[c] The sum of torsional and conformational contributions is 1.0 kcal mol^{-1}.

TABLE VI CALCULATED ENTHALPIES OF FORMATION OF AZO AND AZOXY COMPOUNDS

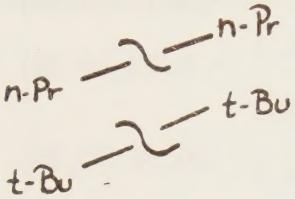
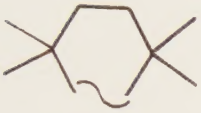
COMPOUND	$\Delta H^{o}_{f}(g)$/kcal mol AZO	$\Delta H^{o}_{f}(g)$/kcal mol AZOXY	$\Delta(\Delta H^{o}_{f}(g))$/kcal mol^{-1} (AZO-AZOXY)
	~N=N~	~N-N(=O)~	
	11.74	- 7.20	18.94
	-7.71	-25.84	18.13
	10.89	-5 .35	16.24
	8.60	- 6.37	14.97
	49.65	30.66	18.99
	40.52	21.39	19.13
	71.83	53.95	17.88
	72.66	53.50	19.16

TABLE VII STRAIN ENERGIES OF AZO AND AZOXY COMPOUNDS (in kcal mol^{-1}) [a]

COMPOUND	AZO =N=N	AZOXY =N-N(=O)	AZO-AZOXY
n-Pr—N=N—n-Pr	0.47[b]	1.21[b]	-0.74
t-Bu—N=N—t-Bu	1.00	2.58	-1.58
	3.08	6.34	-3.26
	6.36	11.07	-4.71
	13.89	14.58	-0.69
	10.35	10.90	-0.55
	13.36	15.16	-1.80
	40.10	40.42	-0.32

a) Defined in the text.

b) The sum of torsional and conformational contributions is 1.0 kcal mol^{-1}.